Thermodynamic Modeling of Gas-Phase *PVTx* Properties for the Ternary R-32/125/143a System[1]

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ABSTRACT

A ternary refrigerant R-32/125/143a is suggested to be a promising alternative to replace R-502. However, there are a few reports on the thermodynamic properties especially of the ternary R-32/125/143a system. Therefore, we aimed to develop a thermodynamic model of the gas-phase *PVTx* properties for R-32/125/143a in terms of a truncated virial equation of state. It is developed on the basis of the experimental *PVTx* property data which were obtianed by a group of the present authors. The experimental *PVT* properties were measured for R-32 by Qian et .[1], for R-125 by Ye et al.[2], and for R-143a by Zhang et al.[3]. The *PVTx* properties for the binary R-32/125 and R-125/143a systems were reported by Zhang et al.[4, 5] and those for R-32/143a by Mizote and Watanabe[6], respectively, whereas those for the ternary R-32/125/143a system were then reported by Tada et al.[7] and Kayukawa et al.[8]. The present model represents these input data with high reproducibility, i.e., within ±0.15% in pressure for each pure component, ±0.25% for binary mixtures except for R-32/143a, and ±0.3% for ternary mixtures, respectively. The present model covers a wide range of temperatures 300-380 K, pressures up to 4.5 MPa, and densities up to 2.5 mol• dm^{-3} at any composition of the present ternary system. The uncertainty of the present model is considered being within ±0.3% in pressure, and ±0.3% in the second virial coefficients. The thermodynamic behaviors of the specific isobaric heat capacity, isochoric heat capacity and speed of sound are also discussed in addition to the examination of temperature dependence of the second and third virial coefficients.

1. INTRODUCTION

It is a pressing subject to reveal the fundamental thermodynamic properties of promised refrigerant mixtures which are expected to replace CFCs and HCFCs.

An azeotropic refrigerant mixture, R-502 [R-22/115 (63/37 mass%)], has been used widely in low temperature application, and its replacement is now in progress. Among the candidates to substitute for R-502, essential thermodynamic properties of typical HFC blended mixtures such as R-507A [R-125/143a (50/50mass%)] or R-404A [R-125/134a/143a (44/4/52mass%)] have been studied rather extensively. Regarding the ternary R-32/125/143a system, however, there exist only a very limited number of reliable sets of measured data; the VLE properties[9, 10] and *PVTx* properties in the liquid phase [10] are only available.

In the present study, therefore, we aimed to develop a thermodynamic model which represents the gas-phase *PVTx* properties of this important ternary system on the basis of the experimental data in an entire range of compositions including each single component, and their binary mixtures obtained by a group of the present authors. Namely, the experimental *PVT* properties were measured for R-32 by Qian et .[1], for R-125 by Ye et al.[2], and for R-143a by Zhang et al.[3]. The *PVTx* properties for the binary R-32/125 and R-125/143a systems were reported by Zhang et al.[4, 5] and those for R-32/143a by Mizote and Watanabe[6], respectively, whereas those for the ternary R-32/125/143a system were then reported by Tada et al.[7] and Kayukawa et al.[8].

2. FUNCTIONAL FORM

The model has a form of the truncated virial equation of state given in Eq. (1). Z and ρ denote the compressibility factor and the molar density, respectively.

$$Z = 1 + \sum_i^3 \sum_j^3 x_i x_j B_{ij} \rho + \sum_i^3 \sum_j^3 \sum_k^3 x_i x_j x_k C_{ijk} \rho^2 + \sum_i^3 x_i D_i \rho^3 \qquad (1)$$

x stands for the mole fraction, whereas each subscript, i, j and k, indicates an arbitrary single component. B and C denote the second and third virial coefficients expressed in terms of the reduced temperature, $T_r = T/T^*$, where T^* is equivalent to the critical temperature for pure component. The characteristic temperature, T^*, is used for the binary and ternary mixtures defined by Eqs. (2) and (3) for B_{ij} and C_{ijk}, respectively. The subscript C denotes the critical point of pure refrigerant.

$$T^* = \sqrt{T_{C,i} T_{C,j}} \qquad (2)$$

$$T^* = \sqrt[3]{T_{C,i} T_{C,j} T_{C,k}} \qquad (3)$$

The second virial coefficient, B_{ij}, and the third one, C_{ijk}, are formulated by following correlations.

$$B_{ij} = b_{1,ij} + b_{2,ij} \tau_{ij}^{-1} + b_{3,ij} \exp\left(\tau_{ij}^{-1}\right) \qquad (4)$$

$$C_{ijk} = c_{1,ijk} + c_{2,ijk} \tau_{ijk}^{-k_{1,ijk}} + c_{3,ijk} \tau_{ijk}^{-k_{2,ijk}} \qquad (5)$$

For the excess virial coefficients such as B_{23} or C_{112}, the critical temperature

values used for the reduced temperature convesion are substituted by the pseudocritial temperatures given in Eqs. (4) and (5).

Note that for each subscript, the relations of ij = ji or ijk = ikj = jik = jki = kij = kji hold. It should also be noted that i = j or i = j = k denotes pure component, while i,j• k, i• j,k, i,k• j corresponds to represent either the excess second or third virial coefficients in Eqs (4) and (5). The quantity with the subscript 1, 2 and 3 represents the pure component R-32, R-125 and R-143a, respectively.

Since the applicable density range of the present model is up to 2.5 mol• dm^{-3}, the fourth and higher virial terms are truncated except for each pure component. The fourth virial coefficient for pure component, D_i, is expressed as a simple cubic function of the reduced temperature, T_r, given in Eq. (6).

$$D_i = d_i T_r^{-3}$$

(6)

3. DETERMINATION OF NUMERICAL CONSTANTS

For the determination of numerical constants for the second, third and fourth virial coefficients for the single components such as B_{11}, C_{222} or D_3, 95 points of the gas-phase *PVT* properties for R-32 obtained by Qian et al.[1], 93 points for R-125 by Ye et al.[2] and 92 points for R-143a by Zhang et al.[3] were selected as input data. The numerical constants for the virial terms in Eqs. (2), (3) and (6) for each single component were determined by introducing these input data into our model, and then applying our optimum least-squares fitting procedure of the present model to the input data.

By using these virial terms for the single components thus optimized, the

excess second and third virial coefficients were correlated by the same fitting procedure to three different input data for the binary mixtures. Namely, the numerical constants for the virial terms, B_{12}, C_{112} and C_{122}, were obtained by employing 124 input data of the gas-phase *PVTx* properties for the binary R-32/125 system, reported by Zhang et al.[4], with an aid of the application of the optimized virial terms for R-32 and R-125 described above. B_{23}, C_{223} and C_{233} correlation were optimized in the same way based on 220 points of gas-phase *PVTx* properties for R-125/143a obtained by Zhang et al.[5]. These input data for the binary R-32/125 and R-125/143a systems, and those for each single component were obtained by the Burnett measurements in our laboratory, whereas 123 *PVTx* properties for the binary R-32/143a system, which were used for the present optimization of B_{13}, C_{113} and C_{133}, were obtained by means of a constant volume apparatus with isothermal expansion by Mizote and Watanabe[6].

By introducing these virial terms for each single component and binary mixtures into our model, the numerical constants for the excess third virial coefficient, C_{123}, were obtained with our fitting of the present model to a total of 220 points of the input data at 4 different compositions, i.e., (10/45/45 mass%), (20/30/50 %), (33/34/33 mass%) and (20/60/20 mass%) for the ternary R-32/125/143a system [7, 8]. All the numerical constants for Eqs. (2), (3) and (6) are tabulated in Table I, together with the critical temperature values for each pure component [11, 12].

4. DISCUSSION

Figure 1 illustrates the relative pressure deviations of all the input data from the calculated pressures by the present model at the corresponding temperatures and densities. It is apparent that the present model represents most of the pure component

data with an excellent accuracy, i.e., within ±0.20% in pressure, while the data for pure

R-125 deviates by +0.26% in maximum. It is also found that the reproducibility of our

model for the binary and ternary mixtures is within±0.3% in pressure. These facts

confirm that the present model has an excellent *PVTx* reproducibility in the entire range

of compositions.

The temperature dependence of the second virial coefficients, B_{11}, B_{22}, B_{33}, B_{12},

B_{23}, and B_{13}, calculated from the present model are shown in Fig. 2 where the present

experimental values and reported second virial coefficients for each pure component are

also included. It should be noted that the experimental values of the second and third

virial coefficients are obtained by the least-squares fitting of the right-hand side of Eq.

(7) to a simple linear function of density along respective isotherms.

$$\frac{Z-1}{\rho} = B + C\rho \qquad (7)$$

It is obvious that both the second virial coefficients for single components and

the excess second virial coefficients show a thermodynamically rational behavior. Each

plot of the experimental value for single component, B_{11}, B_{22} and B_{33}, agrees well with

the calculated curve by the present model. These calculated curves for B_{22} and B_{33} also

agree well with the reported values by Gillis[13] and Beckermann and Kohler[14] as far

as in the applicable range of temperatures from 300 to 380 K, although the deviations of

the B_{33} values by Beckermann and Kohler become more significant at lower

temperatures. In order to examine the reproducibility of the present model for the

second virial coefficients, relative deviations of the experimental second virial

coefficients from those calculated from the present model are illustrated in Fig. 3, where

the experimental values for R-32/125 (20/80mass%) and (40/60mas%) reported by Kiyoura et al.[15] are included. It is found that all the experimental second virial coefficients are excellently represented within ±0.15% for pure components, ±0.20% for binary mixtures and ±0.25% for ternary mixtures, respectively. The available experimental values for R-32/125 by Kiyoura et al.[15] agree well with both the present model and the input experimental data by Zhang et al.[4], within ±0.7% at applicable temperatures of the present model from 330 to 400 K, although their deviation becomes more significant at higher temperatures. The deviations of the excess second virial coefficient, B_{12} and B_{23}, reported by Weber and Defibaugh[16] from the present model vary from 2.9% to 5.8%, which are recognized being satisfactorily small, since the excess second virial coefficients were not obtained directly from the $PVTx$ property measurements for the mixtures. The experimental second virial coefficients for the binary R-32/143a system were not obtained in this work, since there were only 3 or 4 data points along each isotherm, and these are not sufficient to determine the experimental second virial coefficient precisely.

To confirm the thermodynamic consistency of the present model, derived properties such as isochoric heat capacities, C_V, isobaric heat capacities, C_P, and speed of sounds, w, calculated from the present model are discussed in this paper. These properties are calculated by following Eqs. (8) through (10) where R denotes the gas constant.

$$C_V = C_P{}^0 - R \int_0^\rho \frac{T}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2} \right)_\rho d\rho \qquad (8)$$

$$C_P = C_V + \frac{T\left(\dfrac{\partial P}{\partial T}\right)_{\rho}^{2}}{\rho^{2}\left(\dfrac{\partial P}{\partial \rho}\right)_{T}}$$ (9)

$$w = \sqrt{\frac{C_P}{C_V}\left(\frac{\partial P}{\partial \rho}\right)_{T}}$$ (10)

Ideal gas heat capacity, $C_P{}^{0}$, is given in Eq. (11) for which numerical constants were obtained by Ogawa and Sato[17] for each single component given in Table II.

$$\frac{C_P{}^{0}{}_{i}}{R} = \sum_{k=0}^{3} a_{k,i}\, T_{r}{}^{k}$$ (11)

Figures 4, 5 and 6 illustrate the temperature dependence of C_V, C_P and w for the ternary R-32/125/143a (10/45/45 mass%) system. It is apparent that the present model shows a thermodynamically consistent behavior for these derived properties in an extensive range of pressures up to 8 MPa, and temperatures from 200 to 500 K. This fact confirms the thermodynamic consistency of our model not only in the input data range to develop the present model but also in the extended range of temperatures and pressures for the gas-phase R-32/125/143a.

Due to a page limitation, we exclude the discussion on the third virial coefficient although the present model also exhibits an excellent representation of the third virial coefficient with a thermodynamically sound behavior as far as the temperature range of the input data is concerned.

5. CONCLUSION

The thermodynamic model that represents the *PVTx* properties in the gaseous phase of the ternary R-32/125/143a system has been developed in this work. The present model has a form of the truncated virial equation of state, and the numerical constants for its virial terms were obtained on the basis of the experimental *PVTx* data in the entire range of compositions including each binary mixture and single component. The reproducibility of the present model has been confirmed to be satisfactory, within ±0.3% both in pressure and second virial coefficients. The range of validity of the present model was subject to the range of the input data, i.e., densities up to 2.5 mol• dm^{-3}, pressures up to 4.5 MPa, and temperatures 300-380 K in an entire composition of the ternary R-32/125/143a system. The temperature dependence of the derived properties, C_V, C_P and w, as well as that for the second and third virial coefficients were also confirmed to behave thermodynamically rational.

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Table I. Numerical constants in Eqs. (2), (3) and (6)

ij	$b_{1,ij}/\mathrm{dm^3 \cdot mol^{-1}}$	$b_{2,ij}/\mathrm{dm^3 \cdot mol^{-1}}$	$b_{3,ij}/\mathrm{dm^3 \cdot mol^{-1}}$
11	2.953892×10^{-1}	7.115033×10^{-1}	-4.428261×10^{-1}
22	4.180144×10^{-1}	2.628148×10^{-1}	-3.498170×10^{-1}
33	4.324401×10^{-1}	9.356728×10^{-1}	-6.075998×10^{-1}
12	3.904362×10^{-1}	5.307931×10^{-1}	-4.201338×10^{-1}
23	4.476388×10^{-1}	1.199246×10^{-1}	-3.112357×10^{-1}
13	3.574865×10^{-1}	-6.305227×10^{-2}	-1.923525×10^{-1}

ijk	$c_{1,ijk}/\mathrm{dm^6 \cdot mol^{-2}}$	$c_{2,ijk}/\mathrm{dm^6 \cdot mol^{-2}}$	$c_{3,ijk}/\mathrm{dm^6 \cdot mol^{-2}}$	$k_{1,ijk}$	$k_{2,ijk}$
111	1.156706×10^{-2}	1.059520×10^{-2}	-2.468411×10^{-3}	7	10
222	1.203541×10^{-3}	2.593338×10^{-2}	-1.103833×10^{-3}	2.5	13
333	1.630541×10^{-2}	1.886313×10^{-2}	-8.411061×10^{-4}	5	12
112	1.300696×10^{-2}	7.128677×10^{-3}	-3.232567×10^{-4}	7	14
122	-8.097871×10^{-3}	3.451074×10^{-2}	-2.878990×10^{-4}	2.5	12
223	6.228510×10^{-3}	4.545076×10^{-2}	-2.183036×10^{-2}	5	7
233	6.538272×10^{-3}	7.530236×10^{-2}	-5.037317×10^{-2}	5	6
113	8.442775×10^{-4}	2.734839×10^{-2}	-4.804706×10^{-3}	4	8
133	4.398368×10^{-3}	2.606075×10^{-2}	-3.180763×10^{-4}	3	12
123	5.244248×10^{-3}	1.960900×10^{-2}	-7.896543×10^{-6}	3.5	7

i	$T_{C,i}/\mathrm{K}$	$d_i/\mathrm{dm^9 \cdot mol^{-3}}$
1	351.255 [11]	-1.074352×10^{-3}
2	339.165 [11]	-1.948749×10^{-4}
3	345.860 [12]	-1.791378×10^{-3}

Table II. Numerical constants in Eq. (2)

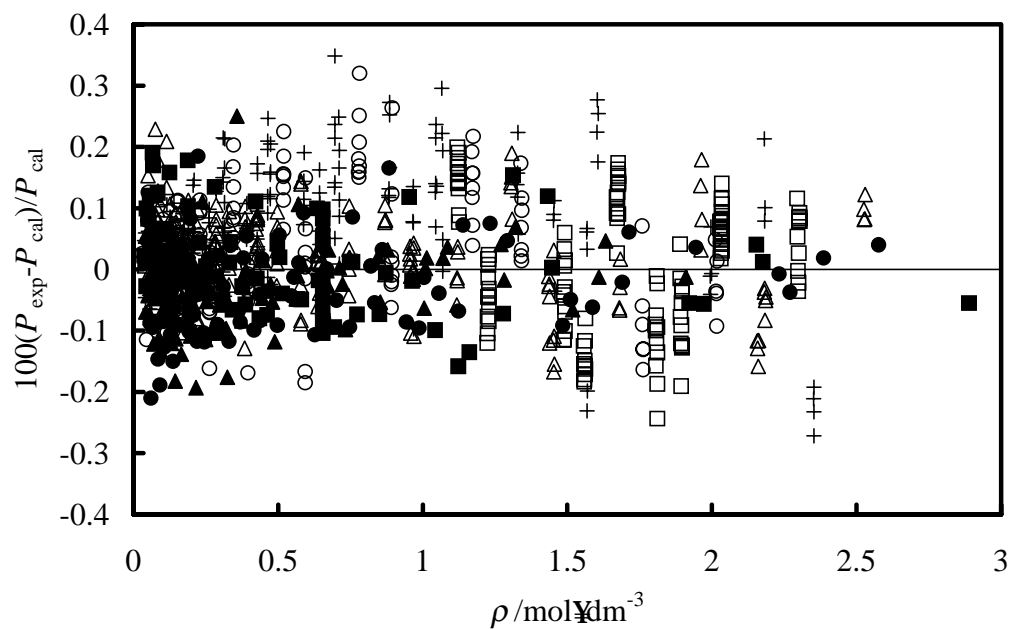| i	a_0	a_1/K^{-1}	a_2/K^{-2}	a_3/K^{-3}
1	4.4971	-2.8987	5.8251	-1.7477
2	3.0164	10.7918	1.2173	-0.3680
3	1.8567	10.14878	-1.4867	-0.1700

FIGURE CAPTIONS

Fig. 1. Relative pressure deviations of input data from the present model for the ternary R-32/125/143a system: ●, R-32; ▲, R-125; ■, R-143a; ○, R-32/125; △, R-125/143a; □, R-32/143a; +, R-32/125/143a.

Fig. 2. Temperature dependence of the second virial coefficients: ●, B_{11}, this work; ▲, B_{22}, this work; ■, B_{33}, this work; △, B_{22}, Gillis[10]; □, B_{33}, Gillis[10]; ○, B_{33}, Beckermann and Kohler[11]; +, B_{12}, Weber and Defibaugh [13]; ×, B_{23}, Weber and Defibaugh [13]; −, calculated curves by the present model.

Fig. 3. Relative deviations of the second virial coefficients from the present model: ●, B_{11}, this work; ▲, B_{22}, this work; ■, B_{33}, this work; △, B_{22}, Gillis[10]; □, B_{33}, Gillis[10]; ○, B_{33}, Beckermann and Kohler[11]; +, B_{12}, Weber and Defibaugh [13]; ×, B_{23}, Weber and Defibaugh [13]; -, B_m, (55/45/0 mol%), Weber and Defibaugh [13]; ◇, B_m, (0/51/49 mol%), Weber and Defibaugh [13]; −, B_m, (0/51/49 mol%), Kiyoura et al. [12].

Fig. 4. Calculated isochoric heat capacities for the ternary R-32/125/143a (10/45/45 mass%) system: ---, saturated vapor; −, ideal gas.

Fig. 5. Calculated isobaric heat capacities for the ternary R-32/125/143a (10/45/45 mass%) system: ---, saturated vapor; −, ideal gas.

Fig. 6. Calculated speed of sounds for the ternary R-32/125/143a (10/45/45 mass%) system: ---, saturated vapor; −, ideal gas.

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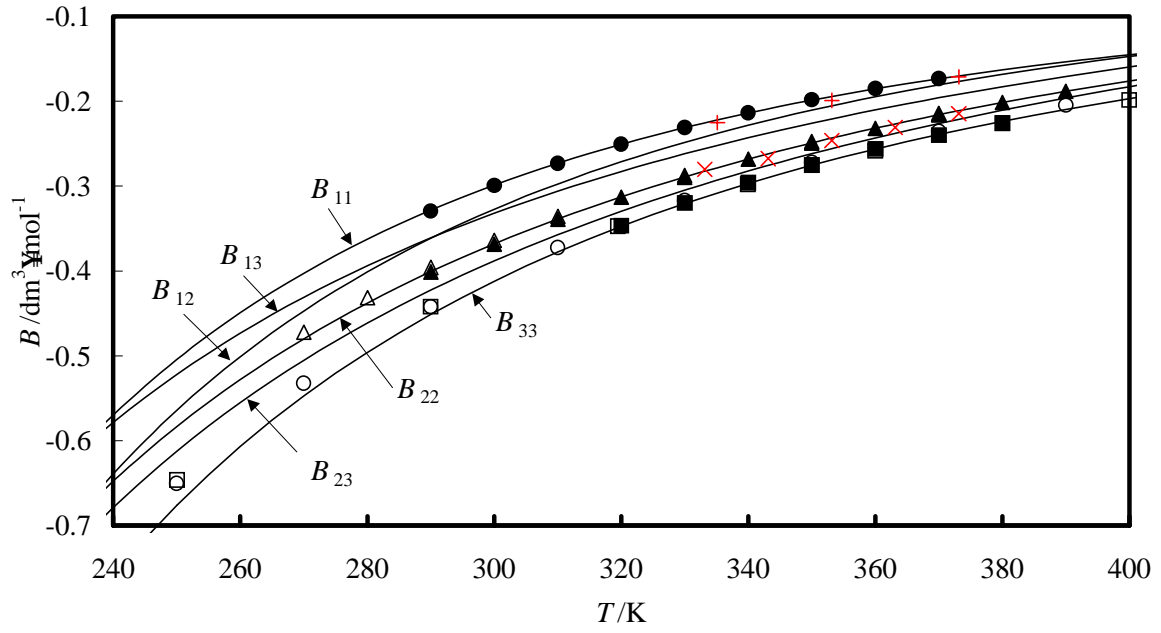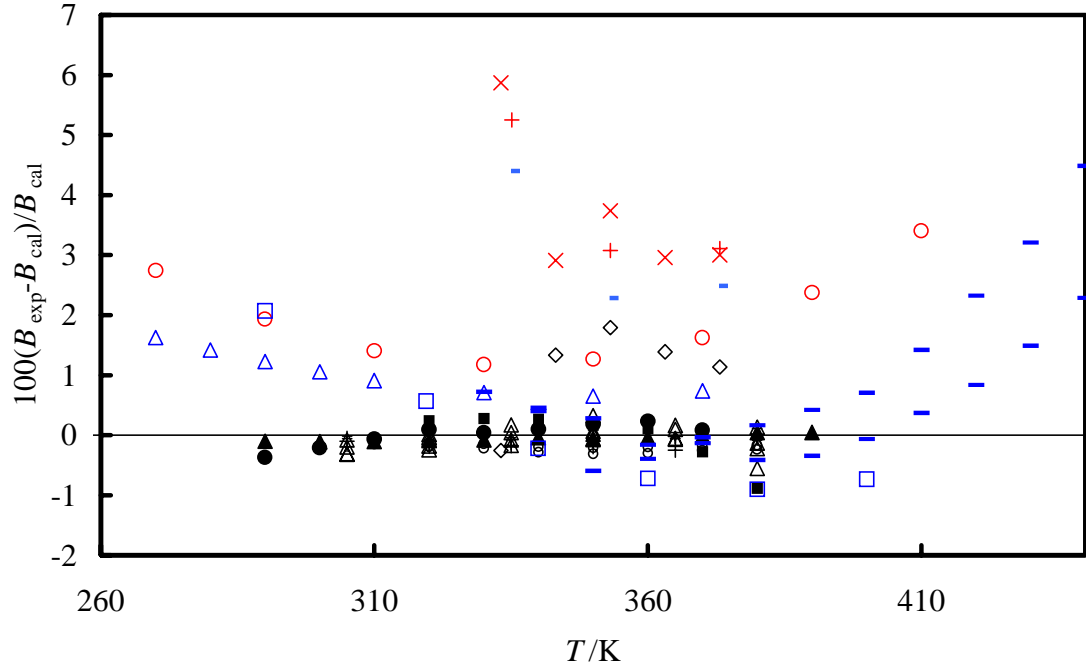
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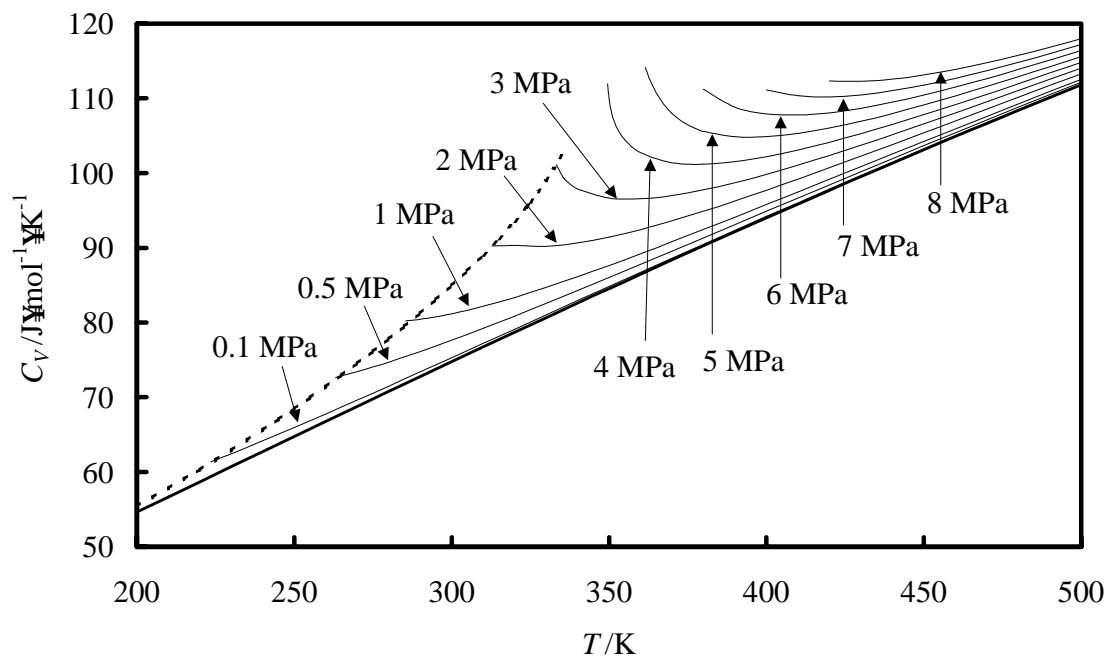
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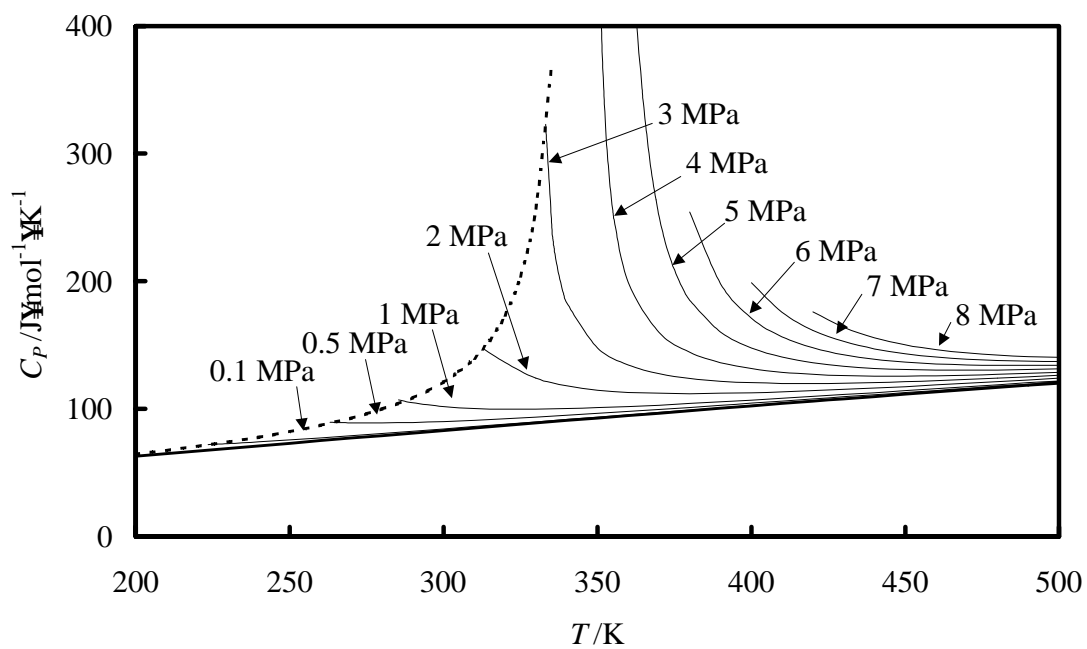
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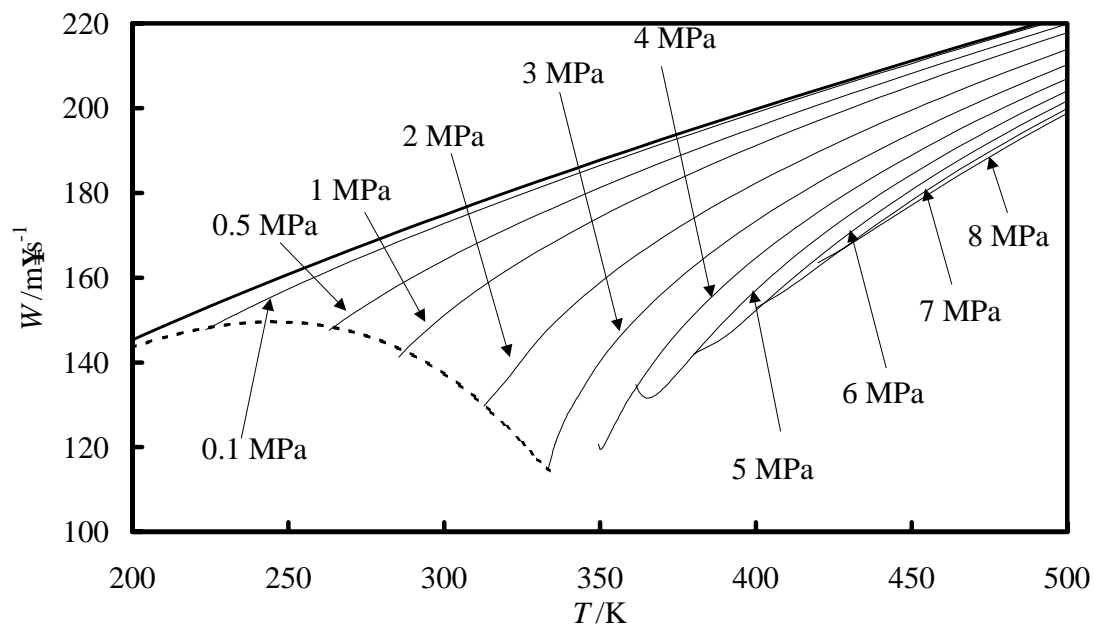
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